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Morphology of Ferroelectric ter(VDF/TrFE/CTFE) Polymers by SAX/WAX

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Beamline(s): X27C

Introduction: New terpolymers of VDF/TrFE/CTFE show large electromechanical strains (4%) in the paraelectric phase as well as large dielectric constants (100) and are promising materials for actuators and thin film capacitors for microelectronics. The incorporation of CTFE introduces defects in the crystals that lower the ferroelectric transition to room temperature that was previously unattainable with VDF copolymers. The cause of the large strain is hypothesized to be the transformation between ferro to para electric crystal phases. Using SAX/WAX scattering, the changes in crystalline phases in the transition region and morphology are measured as a function of terpolymer composition to elucidate the electromechanical strain mechanisms in the amorphous and crystalline phases.

Methods and Materials: The terpolymers of ter(VDF/TrFE/CTFE) were synthesized by the Chung group (Penn State Univ.) using a novel boron catalyst to yield polymers of controlled stoichiometric composition (1). The CTFE concentration in the crystalline phase is key in setting the temperature of the Curie transition. The conformational defect concentration in the crystals is controlled by both chemical composition at synthesis and then by crystallization temperature.

The samples for SAX/WAX data are scanned at 2 ^{o}C /min and the SAX and WAX intensity and intensity profiles are measured every 0.5^{o}C degrees. The SAXS was analyzed and the amorphous region thickness and crystalline lamellae thickness were determined as a function of temperature (26^{o}C to 152^{o}C) including the of the FP and melting transitions for each series of samples. The SAXS intensities were integrated and the total intensity indicated relative changes in density between the amorphous and crystalline regions and especially noted in the transition regions. The WAXS intensity profiles yielded the lattice d-spacing changes and mapped the transition region. The crystalline fractions corresponding to the temperatures scanned were determined and correlated to the SAX data. The changes in the ferro to para transition determined by thermal analysis were then compared to the structural and morphological x-ray results. The ideal melting points were determined both from MDSC scans by melting temperature vs crystallization temperature plots (Hoffman-Weeks plots) and from structural plots of the melting temperature vs reciprocal lamellae thickness (Thompson-Gibbs plots).

Results: Results for the WAX lattice d-spacings are shown in Figure 1 and those for the integrated SAX intensity is shown in Figure 2 for the terpolymer composition 66/22.5/11.5 crystallized at different temperatures (2). As the crystallization temperature is increased, more of the impurities of CTFE are diffused out of the crystal into the surrounding amorphous regions. This enhances the ferroelectric phase of smaller lattice spacing occurring for the higher crystallization temperatures as is shown in Figure 1. The higher crystalline density, as shown in Figure 2, results in an increase of the integrated SAX scattering intensity clearly marking the ferroelectric transition range of 25 ^{o}C to 60 ^{o}C and is well correlated with the d-spacing changes in Figure 1. The crystalline fraction is found to decrease for samples crystallized at higher temperatures. This may illustrate that the nucleated crystals at these temperatures contain only longer segments between defects and those of shorter lengths remain in the amorphous regions. As there are few regions of longer lengths between defects fewer can nucleate and the crystallinity is reduced. Thus the thermal processing conditions to achieve high crystallinities for optimizing the crystal transition mechanism may not be achieved by increasing crystallization temperature.

For the samples of lower VDF content of 59.3 and 55 mole %, the crystalline lamellae thickness increases at lower crystallization temperatures as determined by SAXS data. This thickening is caused by increased volume enthalpy needed by the crystals to overcome the instabilities of the greater concentration of trapped CTFE defects. These results are in agreement with the higher melting temperatures as found by thermal analysis for terpolymers of lower VDF content but thicker lamellae as found by SAXS as discussed above. Both the thermal analysis determined ideal melting points (Hoffman-Weeks plots) and those determined from lamellae thickness (Thompson-Gibbs plots) agree within experimental error. Thus the structural data of SAX/WAX well explain the macroscopic MDSC data. We conclude that it is therefore of importance to verify that the crystal-crystal transition is the major mechanism of the electrostriction and not one in the amorphous regions in order to optimize processing conditions.

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References:

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2) E.Balizer, Z. Wang, A. Petchsuk, B. Hsiao and M Chung. "Structural Relaxations of VDF/TrFE/TCFE Terpolymers," U.S. Navy workshop on Acoustic Transduction Materials and Devices, 14-16 May 2001, Baltimore, MD

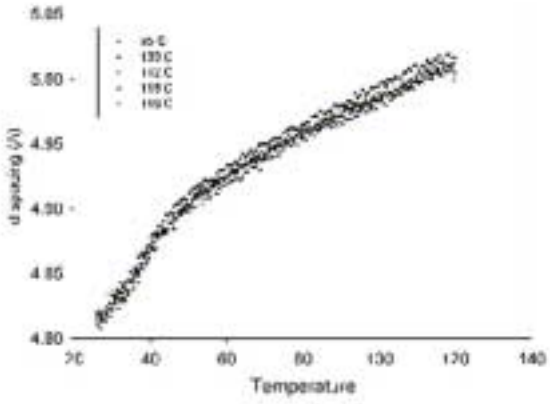

Figure 1. [graph: lattice d-spacing for 66/22.5/11.5 terpolymer for crystallization temperatures of 95C, 100C, 112C, 116C and 118C]

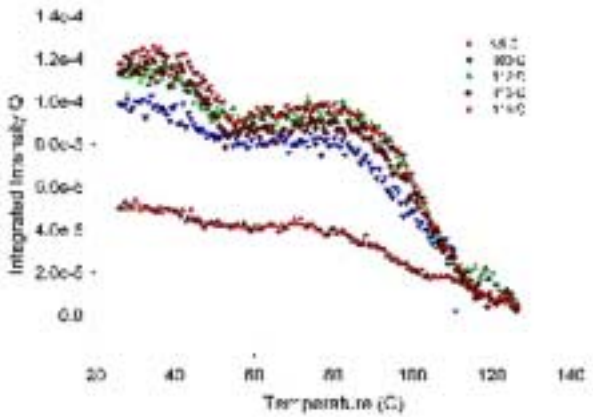

Figure 2. [graph: total integrated small angle scattering intensity for 66/22.5/11.5 terpolymer for crystallization temperatures 95C, 100C, 112C, 116C and 118C]